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A CONVENIENT PREPARATION OF Z-STYRYL, Z,Z- AND E,Z-DISTYRYL SULFIDES IN LIQUID AMMONIA

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Nucleophilic attack of thiols on phenylacetylene (1) in liquid ammonia at room temperature gave the corresponding Z-isomer of styryl sulfides in high yield stereoselectively. Reaction of 1 with Na_2S also proceeded selectively to give Z,Z-distyryl sulfide (12). On the other hand, reaction with NaSH gave 12 besides E,Z-isomer as a minor product.

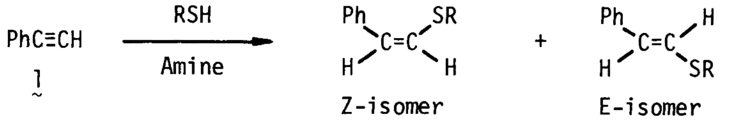
Vinyl sulfides are regarded as one of the synthetic equivalents of carbonyl compounds, and a number of procedures for their preparation have been developed. One of the preparation of vinyl sulfides, which was achieved by Truce and Simms,1) is the direct addition of sulfur nucleophiles to alkynes. It was also shown that thiolate, generated by the thiol-thiolate equilibrium in a basic solvent such as amines, undergoes the trans addition to alkynes.2) These reports and our results3, 4) on a facile synthesis of aryl sulfides by thiols in liquid ammonia urged us to apply the equilibriated system to the preparation of styryl sulfides in liquid ammonia, and we wish to report the convenient one-step synthesis of styryl and distyryl sulfides which uses liquid ammonia as an amine having a low boiling point and small nucleophilicity.

The first attempt was made in the reaction of phenylacetylene 1 with several thiols in liquid ammonia. A typical procedure of the reaction is described below. A solution of 1 (306 mg, 3.0 mmol) and p-chlorophenylmethanethiol 8 (571 mg, 3.6 mmol) in liquid ammonia (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred for 24 h at room temperature. After removal of NH_3, the residue was purified by silica gel column chromatography using hexane-chloroform (1/1 volume ratio) as an eluent to afford the E,Z-mixture of styryl p-chlorobenzyl sulfide (Z/E=10) in 90 % yield.

The results of the reaction of 1 with thiols in liquid ammonia are shown in Table 1. In all the cases, neither disulfides, nor exo-methylenic vinyl sulfides, nor compounds containing amino or imino groups were found in the reaction mixture. Some of the reactions proceeded to form styryl sulfides in high yields with Z-preference caused by the repulsion of vinyl anion with the lone pair of sulfur atom.1) The ratio of Z-/E-isomers of styryl sulfides decreased with increasing size of thiols such as hexanethiol 3, octanethiol 4, and dodecanethiol 5. The reaction of 1 with butanethiol 2 in Et_3N gave styryl butyl sulfide 11 in poor yield compared with that in liquid ammonia (run 1-2 in Table 1).

It was further expected that these procedures would provide us Z,Z-distyryl sulfide 12 by the reaction of 1 with NaSH or Na_2S in liquid ammonia. E,Z-isomer 13 was directly obtained by the reaction of 1 with Na_2S by the use of dibenzo-18-crown-6-ether or $PhCH_2N^+(C_2H_5)_3Cl^-$ reported by Trofimov et al.,5) and both the E,Z- 13 and E,E-isomers of distyryl sulfide were also obtained by

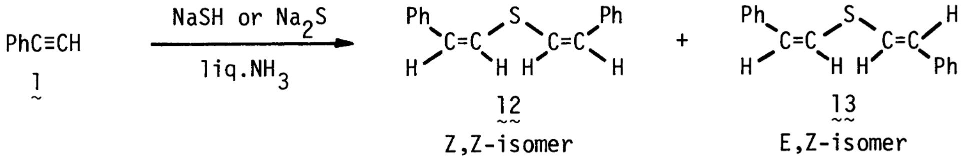
Table 1. Reactions of Phenylacetylene 1 with Thiols [a)]



Run	Thiol		Amine	Time/h	Yield/%	Z/E [b)]
1	C_4H_9SH	2	NH_3	24	71	9.0
2	C_4H_9SH	2	Et_3N	40	27	6.5
3	$C_6H_{13}SH$	3	NH_3	24	93	5.5
4	$C_8H_{17}SH$	4	NH_3	40	80	1.5
5	$C_{12}H_{25}SH$	5	NH_3	40	90	0.80
6	$C_6H_5CH_2SH$	6	NH_3	24	70	10
7	$C_6H_5CH_2SNa$	7	NH_3	18	78	40
8	$p\text{-}ClC_6H_4CH_2SH$	8	NH_3	24	90	10
9	C_6H_5SH	9	NH_3	24	97	0.45
10	$p\text{-}CH_3C_6H_4SH$	10	NH_3	24	95	0.65

a) PhC≡CH 1, RSH : 3 mmol, liq.NH_3 : 10 ml, Et_3N : 2 ml,
Temperature : Room temperature.
b) Determined by ^1H-NMR.

Table 2. Reactions of Phenylacetylene 1 with NaSH or Na_2S in liq.NH_3 [a)]

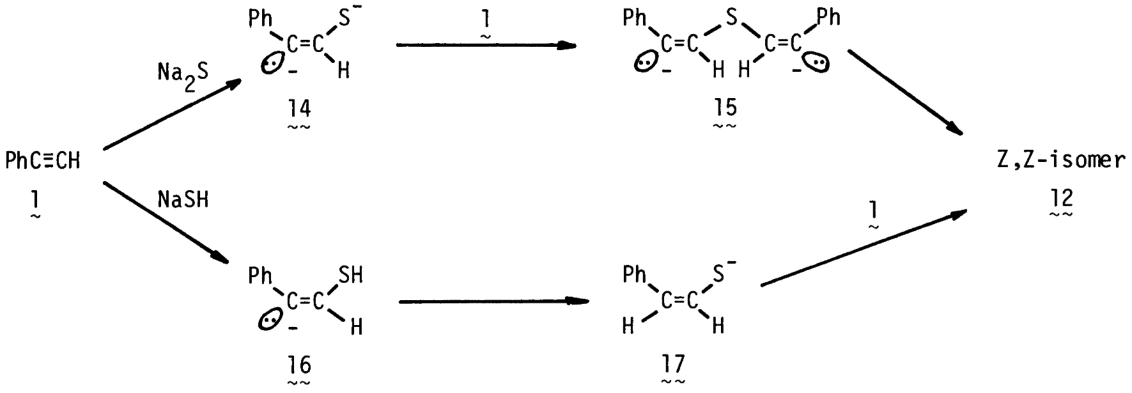


Run	NaSH or Na_2S (mmol)	Yield/%	Z,Z/E,Z [b)]
1	NaSH (5)	67	2.5
2	$Na_2S.9H_2O$ (5)	71	20
3	$Na_2S.9H_2O$ (5) + H_2O (55)	78	10

a) PhC≡CH 1 : 5 mmol, liq.NH_3 : 10 ml, Temperature : 100 °C,
Time : 5 h.
b) Determined by ^1H-NMR.

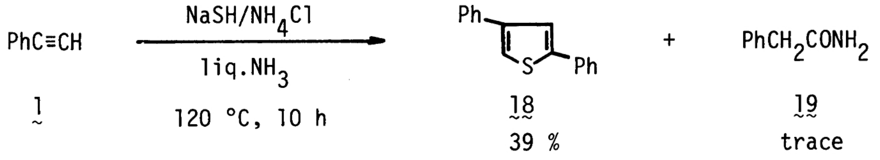
Horner-Wittig reaction.[6, 7)] Aida et al.[8)] have reported that the symmetric and unsymmetric divinyl sulfides were obtained by the elimination of HI by base from α, α'-diiodo sulfides. To 10 ml of liquid ammonia was added 510 mg (5 mmol) of 1 and 1200 mg of $Na_2S.9H_2O$ in a titanium autoclave. The reaction mixture was heated to 100 °C for 5 h with stirring, and after removal of NH_3, the residue was separated by silica gel column chromatography using hexane-chloroform (1/1 volume ratio) as an eluent to afford a colorless needle product, which was determined to be Z,Z-distyryl sulfide 12 (71 %) by its spectral analysis, especially by the symmetrical signal of ^1H-NMR and ^{13}C-NMR.[9)] On the other hand, in the reaction of 1 with anhydrous NaSH in liquid ammonia at 100 °C for 5 h, the mixture of Z,Z- 12 and E,Z-isomer 13 of distyryl sulfide (Z,Z/E,Z=2.5) was obtained in 67 % yield. E,Z-isomer 13 of distyryl sulfide was identified by comparing its spectral and physical data with those of the authentic sample.[7, 10] The reaction of 1 with $Na_2S.9H_2O$ or NaSH in Et_3N under reflux or in autoclave (120 °C) was unsuccessful, which would be due to insolubility of $Na_2S.9H_2O$ and NaSH in Et_3N.

Z,Z-distyryl sulfide 12 obtained by the reaction of 1 with $Na_2S.9H_2O$ or NaSH in liquid ammonia would be formed as shown in the Scheme 1. Na_2S reacted with 1 to afford dianion 14, which further reacted with 1 to give Z,Z-distyryl sulfide dianion 15. Dianion 15 was protonated to give Z,Z-distyryl sulfide 12. On the other hand, NaSH reacted with 1 to give carbanion 16, followed by proton-transfer to give thiolate 17. Thiolate 17 further reacted with 1 to give Z,Z-distyryl sulfide 12.



Scheme 1.

In the reaction of 1 with NaSH in the presence of NH_4Cl in liquid ammonia in a titanum autoclave, 2,4-diphenylthiophene 18 was obtained in moderate yield without contamination of Z,Z- 12 or E,Z-distyryl sulfide 13. The by-product obtained in a trace amount was identified as amide 19 by its physical properties.



Scheme 2.

It is worth noting that the stereoselective preparations of Z-styryl sulfides and Z,Z-distyryl sulfide were established by the reaction of phenylacetylene 1 with thiols and $Na_2S.9H_2O$ in liquid ammonia respectively. Work along with the expansion of synthetic utilities of these vinyl sulfides is in progress in our laboratory.

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9) Z,Z-Distyryl sulfide 12 : colorless needles, mp 33.5-34.5 °C, IR(neat) ; 3010, 1590, 1490, 1345, 910, 835, 770, 720, 690, 675, 520 cm^{-1}, MS(m/e) ; 238(M$^+$), ^{1}H-NMR(CCl_4) ; δ 6.11 (d, 2H, CH, J=11 Hz), 6.35 (d, 2H, CH, J=11 Hz), 7.06-7.41 (m, 10H, Ph), ^{13}C-NMR(CCl_4) ; δ 125.917 (d), 126.638 (d), 127.029 (d), 128.267 (d), 128.596 (d), 136.100 (s), Found : C, 79.81; H, 5.79; S, 13.38%. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45%.

10) E,Z-Distyryl sulfide 13 : colorless plates, mp 96-96.5 °C (lit. 96 °C), IR(KBr) ; 1605, 1590, 1565, 1490, 1445, 1365, 950, 835, 770, 740, 690, 680, 525 cm^{-1}, MS(m/e) ; 238(M$^+$), ^{1}H-NMR(CCl_4) ; δ 6.26 (d, 1H, CH, J=11 Hz), 6.45 (d, 1H, CH, J=11 Hz), 6.48 (d, 1H, CH, J=16 Hz), 6.69 (d, 1H, CH, J=16 Hz), 7.13-7.28 (m, 10H, Ph), ^{13}C-NMR($CDCl_3$) ; δ 123.766 (d), 123.896 (d), 125.854 (d), 127.160 (d), 127.353 (d), 128.267 (d), 129.703 (d), 136.299 (s).

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